

Chapter 3

Theoretical Models

In this chapter, the theoretical concepts necessary for the understanding of the experimental results presented in this work will be described. First, the basic principles of molecular vibrations will be introduced, with an emphasis on the anharmonicities and their effects on the vibrational spectrum. This is followed by a brief description of the excitation mechanism. The mechanisms underlying the infrared photodissociation (IRPD) technique will be presented.

3.1 Introduction to Infrared Spectroscopy

Infrared spectroscopy is widely used for the identification of molecular vibrations, which help for the structure determination of molecular systems. Different structural groups exhibit infrared activity in characteristic regions of the spectrum. By measuring the infrared spectrum of a molecule and by knowing the frequency where these groups absorb radiation, a molecular structure can be proposed. The *fingerprint region*, is the region of the IR spectrum, where, by the absorption of an IR photon, a molecule produces a unique pattern. For the systems which were investigated in this thesis, the fingerprint region extends mainly below 2000 cm^{-1} .

3.2 Theoretical Treatment of Molecular Vibrations

Classically, the vibrational motion of the molecules can be treated approximately considering that the atoms in a molecule are connected with bonds that act like springs undergoing harmonic oscillations about the equilibrium position. In the case

of a two atomic system, the frequency ν of the oscillation is given by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (3.1)$$

where k represents the force constant and μ the reduced mass of the molecule. For two atoms having the masses m_1 and m_2 , the reduced mass is defined as:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3.2)$$

Since the force that acts on the two atoms is the elastic force and it is given by the negative derivative of the potential energy V , the following expression for the harmonic potential is obtained:

$$V = kq^2/2 \quad (3.3)$$

where $q = x_2 - x_1$ represents the displacement of the two atoms from the equilibrium internuclear distance. Equation (3.1) indicates that by changing the reduced mass, the frequency of the vibration can be shifted. For example, this relation is very useful for the assignment of vibrations involving the hydrogen atom stretching motion, where the hydrogen atom can be replaced by deuterium. In this case, a red shift of the vibrational frequency of $\sqrt{2}$ is expected. This is referred to as the *isotope effect* and will be exemplified in Chapter 4.

A better description of the molecular vibrations can be obtained by treating the systems quantum mechanically. For this, the Schrödinger equation for the system of interest needs to be solved:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \hat{H} \Psi(\mathbf{r}, \mathbf{R}, t) \quad (3.4)$$

Equation 3.4 is referred to as the *time-dependent Schrödinger equation*, where $\psi(\mathbf{r}, \mathbf{R}, t)$ represents the molecular wavefunction, which depends on the electronic coordinates \mathbf{r} , the nuclear coordinates \mathbf{R} and time t . \hat{H} represents the Hamilton operator of the system and can be written as the sum of the total kinetic energy of the electrons \hat{T}_e , total kinetic energy of the nuclei \hat{T}_n and the potential energy consisting of the electron-electron \hat{V}_{ee} , electron-nuclei \hat{V}_{ne} and nuclei-nuclei \hat{V}_{nn} Coulomb interactions:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{ne} + \hat{V}_{nn} \quad (3.5)$$

Because in equation (3.5) of the Hamiltonian, the time does not appear explicitly, a separation of variables according to space and time can be performed. Hence, the molecular wavefunction of the system takes the form:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \psi(\mathbf{r}, \mathbf{R}) \cdot \varphi(t) \quad (3.6)$$

By substituting equation (3.6) in equation (3.4), two differential equations are obtained, one time-independent and one time-dependent. The *time-independent Schrödinger equation* for the spatial wavefunction has the form:

$$\hat{H} \psi(\mathbf{r}, \mathbf{R}) = E \psi(\mathbf{r}, \mathbf{R}) \quad (3.7)$$

For the time-dependent differential equation, the following solution is obtained:

$$\varphi(t) = \exp\left(\frac{-iEt}{\hbar}\right), \quad \hbar = \frac{h}{2\pi} \quad (3.8)$$

where E represents the eigenvalue of the Hamiltonian and h the Planck constant.

The solutions of the time-independent Schrödinger equation are difficult to be obtained, especially for large systems. Usually it is possible to introduce the *Born – Oppenheimer approximation*, which considers that the motion of the heavy nuclei is much slower than that of the light electrons. As a consequence, the nuclei can be considered fixed and the wave function can be separated into an electronic and a nuclear part:

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_{el}(\mathbf{r}, \mathbf{R}) \psi_n(\mathbf{R}) \quad (3.9)$$

where $\psi_{el}(\mathbf{r}, \mathbf{R})$ represents the electronic wave function for a given configuration of the nuclei and $\psi_n(\mathbf{R})$ represents the nuclear wavefunction.

The Hamiltonian from equation (3.5) can be separated into an electronic \hat{H}_{el} and a nuclear \hat{H}_n part:

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} \quad (3.10)$$

$$\hat{H}_n = \hat{T}_n + \hat{V}_{nn} \quad (3.11)$$

By introducing the separated wavefunction (3.9) into the time-independent Schrödinger equation, and considering the kinetic energy of the nuclei \hat{T}_n equal to zero and the Coulomb interaction between the nuclei \hat{V}_{nn} constant, the electronic equation is obtained:

$$\hat{H}_{el} \psi_{el}(\mathbf{r}, \mathbf{R}) = E_{el}(\mathbf{R}) \psi_{el}(\mathbf{r}, \mathbf{R}) \quad (3.12)$$

Equation (3.12) describes the electronic motion and can be resolved parametrically with respect to the nuclear set of coordinates \mathbf{R} . The solutions give the electronic energies as a function of the nuclear displacement, defining a potential energy surface (PES). If the electronic problem is solved, it is subsequently possible to approach the nuclear problem.

Solutions to the nuclear Schrödinger equation,

$$(\hat{H}_n + E_{el}(\mathbf{R})) \psi_n(\mathbf{R}) = E \psi_n(\mathbf{R}) \quad (3.13)$$

describe the vibration, rotation and translation of a molecule. E is the Born-Oppenheimer approximation to the total energy and includes the electronic, vibrational, rotational and translational energy.

Returning to the harmonic oscillator treated classically at the beginning of the chapter, now a quantum mechanical explanation can be given. The potential energy V can be expressed in a general form as a power series expansion about the equilibrium position. In the case of the harmonic oscillator, only the quadratic term is considered and the potential energy can be expressed as in equation (3.3). By introducing V in the time-independent Schrödinger equation (3.7) and solving the equation, the allowed energy values E for the harmonic oscillator are obtained:

$$E = \hbar\omega\left(v + \frac{1}{2}\right), \quad v = 0, 1, 2 \dots \quad (3.14)$$

where ω represents the angular frequency. For $v = 0$ the zero point energy $E(0)$ is obtained. Equation 3.14 indicates that for the harmonic potential the vibrational levels are equally separated from each other $\Delta E = E_{v+1} - E_v = h\nu = \hbar\omega$.

The description of the vibrational motion for a two atomic system is rather simple, however polyatomic molecules present a large number of possible vibrations. In some cases, the displacement of an atom along one cartesian coordinate might lead to complicated motions. The representation of these vibrations in cartesian coordinates will result in complicated expressions of the kinetic and potential energy, where not only squared terms but also cross products between the coordinates appear. The choice of other coordinates, referred to as the *normal coordinates*, results in a simplified description of the vibrational motion and allows the description of the kinetic and potential energy as a sum of square terms. The displacement of the system according to these coordinates will lead to a simple motion in which all particles move in phase with the same frequency. The motions along the normal coordinates are referred to as *normal modes*. Any vibrational motion of the system can be represented as a superposition of the normal vibrations with suitable amplitudes. For a molecule with N nuclei there are $3N$ degrees of freedom from which $3N-6$ for nonlinear molecules, respectively $3N-5$ for linear systems are left to describe the vibrational motions of a molecular systems. Accordingly, there are $3N-6$ ($3N-5$) normal coordinates to describe the vibrational motion. The other 6 (5) coordinates describe the rotational and translational motions of the molecule.

Figure 3.1 shows the $3N-5$ (4) possible vibrations of a linear three atomic molecule. The symmetric motion is labeled as ν_1 , ν_2 is the bending motion and ν_3 , the

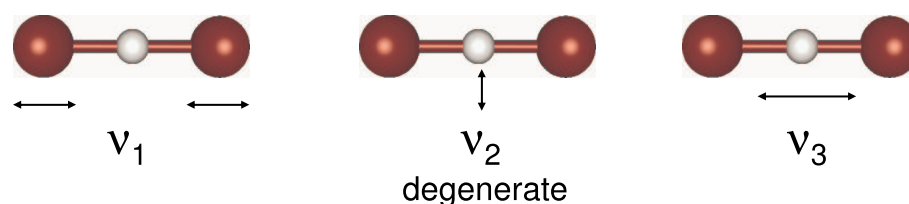


Figure 3.1: The vibrations of a linear three atomic molecule. ν_1 is the symmetric stretch, ν_2 represent the bending mode, ν_3 the antisymmetric stretch. The bending mode presents two vibrations which are perpendicular to each other and have the same energy (are degenerate).

antisymmetric stretch.

According to equation (3.3) the harmonic oscillator is characterized by a parabolic potential curve. This is generally true only for small displacements from the equilibrium distance. The potential energy and the restoring force increase infinitely when increasing the distance from the equilibrium. However, in real systems, at high internuclear distances, the attractive force is zero (the molecule dissociates) and the potential energy has a constant value which represents the dissociation energy. For larger amplitude vibrational motions, anharmonicities play an important role. The deviation from the potential curve described by equation (3.3) to the curve of a real molecule is due to *mechanical anharmonicity*. The simulation of a potential energy surface including the anharmonicities is difficult.

An approximate solution for two atomic system which describes well also the dissociation was given by P. M. Morse.^{66,67} He proposed a general formula for the potential energy as:

$$V = D_e[1 - e^{-a(R-R_e)}]^2 \quad (3.15)$$

In equation (3.15), D_e represents the dissociation energy, R , the internuclear distance, R_e is the equilibrium bond length and the parameter a determines the width of the potential well.

$$a = \sqrt{\frac{\mu}{2D_e}} \omega_e \quad [cm^{-1}] \quad (3.16)$$

$\omega_e = 2\pi\nu_e$ denotes the harmonic vibrational frequency.

The Morse potential accounts for the anharmonicity, which is defined through the parameter χ_e , referred to as the anharmonicity constant. The value of χ_e can be

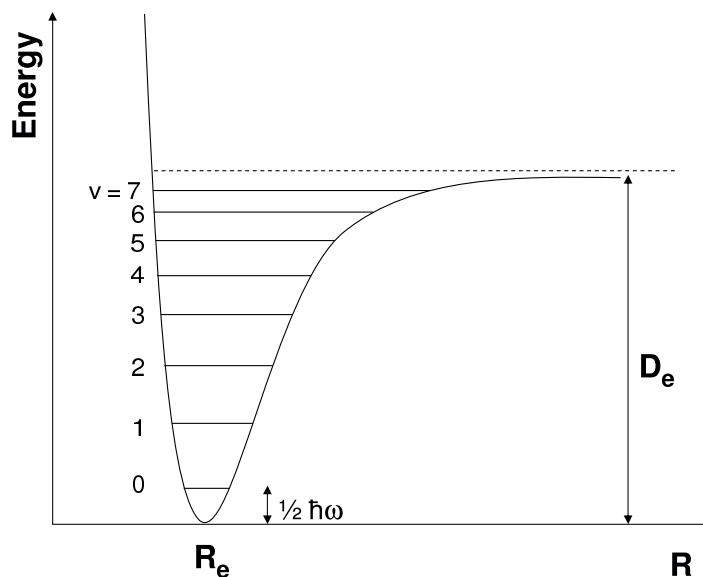


Figure 3.2: Schematic representation of the Morse potential curve for a two atomic molecule. The potential energy is plotted as a function of the bond distance R . R_e , D_e are the equilibrium bond length and the dissociation energy, respectively. The numbers on the left side of the potential denote the vibrational levels $v=0, 1 \dots 7$.

determined by the following equation:

$$\chi_e = \frac{\hbar\omega_e}{4D_e} \quad (3.17)$$

The values of the frequency ω_v for certain vibrational levels can be determined by considering the anharmonicity constant of the potential. Their values can be determined by evaluating the following equation:

$$\omega_v = \omega_e \left[1 - \chi_e \left(v + \frac{1}{2} \right) \right] \quad (3.18)$$

A similar formula to (3.18) can be obtained for the energy levels:

$$E_\nu = \hbar\omega_e \left(v + \frac{1}{2} \right) \left[1 - \chi_e \left(v + \frac{1}{2} \right) \right] \quad (3.19)$$

A schematic representation of a Morse potential curve for a two atomic molecule is shown in Figure 3.2. One of the effects on the anharmonicity can be observed in this figure, where due to a positive anharmonicity constant the distance between the energy levels becomes smaller with increasing the energy.

3.2.1 Interaction with Light

Transitions between vibrational levels can be achieved through interactions of electromagnetic radiation on a molecular system. If the influence of the electromagnetic

radiation is small, it can be treated as a *perturbation*. In the dipole approximation the perturbation is defined as $\hat{H}' = -\hat{\boldsymbol{\mu}} \cdot \mathbf{E}$ and appears as an additional term to the Hamilton operator \hat{H} .

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (3.20)$$

where \hat{H}_0 represents the unperturbed Hamiltonian. In this approximation, the molecule-field interaction is reduced to that of the dipole moment $\hat{\boldsymbol{\mu}}$ of the molecule with the time-dependent electric field of the laser \mathbf{E} .

Within the electric dipole approximation, a molecule is allowed to absorb radiation at the transition $i \rightarrow j$ only if the transition non-diagonal matrix element of its dipole-moment operator is different from zero:

$$\langle j | \hat{\boldsymbol{\mu}} | i \rangle \neq 0 \quad (3.21)$$

Considering small vibrations, the vibrational dipole moment of a molecule can be written as an expansion by the normal coordinates q_i . In a first approximation, this change can be considered linear:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial \boldsymbol{\mu}}{\partial q_i} \right) q_i + \dots \quad (3.22)$$

$\boldsymbol{\mu}_0$ represents the permanent dipole moment of the studied system associated with the equilibrium configuration.^a

If the second term in equation (3.22) is non-vanishing, the vibration is referred to as *infrared active*. In the opposite case, the vibration will be *infrared inactive*. For the linear molecule presented in Figure 3.1, the symmetric vibration ν_1 is infrared inactive, since there is no change of the dipole moment as the molecule vibrates. Due to the same reason, homonuclear diatomic molecules show no infrared activity.

By using the equations (3.22) and (3.21), it can be shown that the selection rule for infrared transitions in the case of the harmonic oscillator is $\Delta v = \pm 1$. The line intensity for vibrational bands is predominantly proportional to the square of the vibrational dipole moment $\left(\left(\frac{\partial \boldsymbol{\mu}}{\partial q_i} \right)^2 \right)$. The anharmonicity gives rise to a change of the selection rule to $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ which leads to the appearance of overtones ($n\nu_i$). Usually, the anharmonicity is small and the intensity of the overtones is low.

In polyatomic molecules the form of the potential is more complicated. The power series expansion of the potential energy will contain also higher terms than

^aThe appearance in the equation of the Taylor expansion of the dipole moment (3.22) of higher terms in q_i represents another aspect of the anharmonicity. This is referred to as the *electrical anharmonicity*.

the quadratic considered for the harmonic case. By introducing this potential energy in the time-independent Schrödinger equation (3.7) the following vibrational terms ($G(v_i) = E(v_i)/hc$) for non-degenerate vibrations are obtained:

$$\sum_i G_{v_i} = \sum_i \omega_i(v + \frac{1}{2}) + \sum_{i \leq j} \chi_{ij}(v_i + \frac{1}{2})(v_j + \frac{1}{2}) + \dots \quad (3.23)$$

where ω_i represents the fundamental vibration wavenumber for infinitely small displacements (analogous to ω_e for diatomic molecules) and χ_{ij} are the anharmonic constants, which can have positive or negative values. One effect of the anharmonicity in polyatomic molecules is the mixing of vibrational normal modes. This can lead to the appearance of combination bands ($\nu_i \pm \nu_j$) in the infrared spectrum. The intensity of these bands is generally small in comparison to the fundamental excitations. An exception arises when two levels with the same symmetry, for example, an overtone and a fundamental are very close in energy (accidental degeneracy), referred to as *Fermi resonances*. Due to the perturbation of the energy levels, the near degeneracy is lifted and two separate bands with perturbed intensities appear in the spectrum. For example, an overtone band might "borrow" intensity from the fundamental and it will show up in the spectrum more intense than in the case when no Fermi resonance occurs. The same effect can be observed in the case of combination bands. The combination bands can be either summation ($\nu_l + \nu_k$) or difference bands ($\nu_l - \nu_k$). Difference bands appear when the initial state is not the ground state $v = 0$. The summation and the difference bands should have the same intensity. However, due to the Boltzmann distribution, the population in a higher excited state is lower than in the ground vibrational state and therefore the intensity of the difference bands will be smaller.

Because of these possible complications in the experimental infrared spectra, the evaluation and assignment of the vibrational frequencies of polyatomic molecules especially with high anharmonicities is difficult and, in these cases, high level anharmonic calculations are necessary.

Due to the mainly low densities of molecules in the gas phase, direct absorption infrared spectroscopy in the gas phase is known to have a low sensitivity. In the direct absorption infrared spectroscopy, the amount of absorbed or transmitted radiation is measured. According to the Lambert-Beer law the absorbance (A) of the sample is given by:

$$A = \log \frac{I}{I_0} = \epsilon cl \quad (3.24)$$

I is the intensity of the transmitted light and I_0 represents the intensity of the incident light.

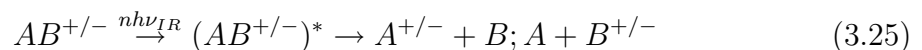
Here, ϵ represents the molar absorption coefficient, c the concentration and l the light path length. In the experiments presented in this thesis the maximum number of ions per cm^3 is limited by the space-charge limit equal to $10^8 \text{ ions}/cm^3$, l is equal to the trap length (20 cm) and $\epsilon = 10^4 \text{ M}^{-1}cm^{-1}$. Considering the above values, a change in the light intensity of $3.2 \cdot 10^{-8}$ is expected. This value is too low to be detectable. Therefore, other methods are necessary for the measurement of the infrared spectra of ions in the gas-phase.

3.3 Excitation Mechanisms

Since for IR investigations of gas phase ions, direct absorption infrared measurements are often not sensitive enough, *action spectroscopy* methods have been developed. The action spectroscopy relies on the detection of an effect ("action") which was produced by the interaction of the molecules with the radiation.

3.3.1 Infrared Photodissociation Spectroscopy (IRPD)

One possibility of action spectroscopy is the measurement of the photodissociation yield formed as a consequence of infrared photon absorption as shown schematically in expression 3.25:



This process is referred to *infrared photodissociation* (IRPD) and for charged systems presents a high sensitivity, since detectors are able to detect single ions. IRPD can proceed by two absorption schemes: a) a *coherent stepwise* absorption mechanism and b) an *incoherent sequential* absorption mechanism. Coherent stepwise IRPD occurs via "ladder climbing" up the energy levels of an oscillator. The efficiency of stepwise absorption depends on the anharmonicity of the potential. At high energies, the excitation source is non-resonant with the anharmonic levels (anharmonic bottleneck effect) and the "ladder climbing" mechanism is prohibited (see Figure 3.3). Thus, for systems with high dissociation energies of few eV the coherent stepwise absorption will fail to induce dissociation at the excitation energies and pulse intensities used in the experiments presented in this thesis.

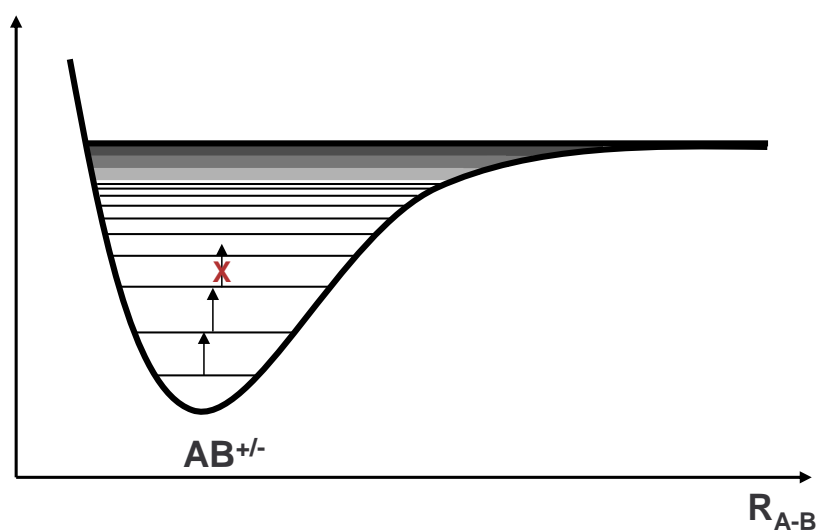


Figure 3.3: Schematics of the "ladder climbing" mechanism. After few transitions, vibrational anharmonicity hinders further resonant absorption of photons.

The most likely mechanism for IRPD with FELIX is the sequential incoherent absorption mechanism shown in Figure 3.4. This mechanism can be divided into three regions. The first region is characterized by a low density of states where the energy levels are well separated. In this region the effect of the anharmonicity is small⁶⁸ and one or few photons can be resonantly absorbed. This is followed by internal vibrational redistribution (IVR) which proceeds via anharmonic coupling. The IVR process de-excites the absorbing vibrational state by redistributing the energy into the quasicontinuum of ro-vibronic states. The quasicontinuum (Region II) is characterized by a high density of mutually interacting states. The de-excited vibrational state may absorb new photons followed again by a redistribution of the energy. Further photons are absorbed until the photodissociation threshold is reached. In the last region, which is characterized by a continuum of states, photodissociation occurs and fragment ions are produced. The photodissociation occurs typically through the lowest energy dissociation channel. If the laser fluence is high enough, dissociation through several channels might occur.^{69,70}

The process by which energy flows into and breaks a weak bond after the excitation of the chromophore, is known as *vibrational predissociation* (VPD).⁷¹ The limitation of this method is that it is only useful for probing transitions that terminate above the ion's dissociation threshold which is mostly a multiphotonic process. In the literature often the term vibrational predissociation spectroscopy is referred to the messenger atom technique (see the following subsection), although in both methods dissociation occurs through vibrational predissociation. Therefore, in this thesis, the experiments

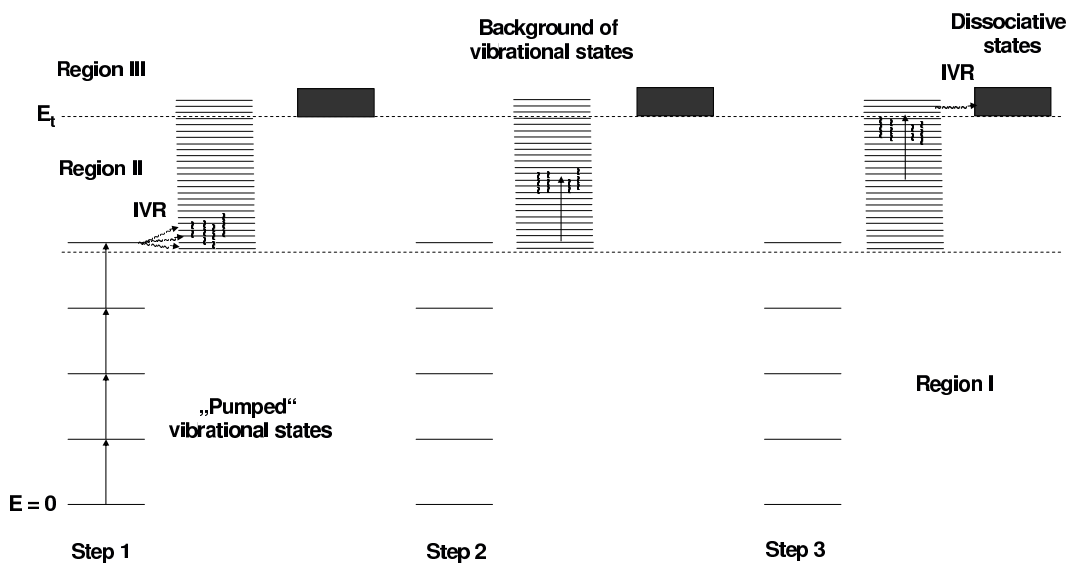


Figure 3.4: The sequential incoherent absorption mechanism. Resonant absorption of few infrared photons in region I is followed by internal vibrational redistribution (IVR) of the energy in other vibrational modes. Region II is characterized by the quasicontinuum, where there is always a possible resonant transition. Further photons are absorbed until the photodissociation threshold (E_t) is reached. Region III is the characterized by a continuum of states where photodissociation occurs. Adapted from Mukamel and Jortner.⁶⁸

performed with the messenger atom technique are referred to as VPD and the experiments on the uncomplexed ions, which generally require multiphoton absorptions, are referred to as IRMPD (infrared multiphoton photodissociation spectroscopy).

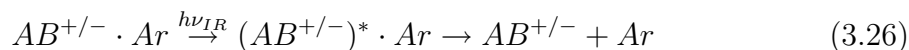
The incoherent multiphoton absorption mechanism depends on the density of vibrational states. Consequently, it is expected to be more efficient for large systems.⁷² In small molecules, with a low density of vibrational states, the anharmonic bottleneck effect is bigger and higher laser intensities are necessary for the same amount of absorbed laser energy.

After dissociation, most of the excess energy will remain as internal energy in the fragments, only a small fraction being released as translational energy. For large molecules the dissociation fragments may already be excited in the quasi-continuum and dissociate again. Secondary or sequential dissociation is very probable in multiphoton photodissociation (MPD) experiments at high laser fluence, especially in large systems. Competing dissociation channels might be opened, if their energy is close to the lowest dissociation channel.

Messenger atom technique

The number of absorbed photons can be substantially lowered when a weakly bound "spy" atom is attached to the ion. Ideally, this spy atom does not perturb the structure and the vibrations of the "core" ion, but it can be detached by the absorption of one or few photons.⁷¹ A second advantage of this method is that the attachment of a weakly bound atom adds low frequency vibrations which increase the density of states and promote IVR and dissociation rates.⁷² This method is referred to as the *messenger (spy) atom technique*. The vibrational predissociation mechanism here relies on the loss of the messenger atom or molecule, after the excitation of the chromophore vibrational resonance.

The basic concept of the *Ar* dissociation mechanism is shown in equation 3.26.



The core ion $AB^{+/-}$ is excited by resonant absorption of one or few photons (much less than required for the uncomplexed ion). The absorbed energy will be eventually redistributed through IVR leading to thermal heating of the molecule and to the dissociation of the weakest bond, in this case dissociation of the *Ar* atom. The time the energy needs to be redistributed depends on the coupling constants to the van der Waals mode. Since the coupling to the *Ar* atom is low, the time that the energy remains localized in the $A - B$ bond is long. Based on the Heisenberg relation $\Delta E \approx h/\Delta t$, the width of the transition is small resulting in sharp features in the IR spectra.

In this work the predissociation of $(BrHBr)^- \cdot Ar$ and $(BrDBr)^- \cdot Ar$ as well as $BrHI^- \cdot Ar$ and $BrDI^- \cdot Ar$, was measured. The *Ar* atom is only weakly bound to the ion ($\approx 300 \text{ cm}^{-1}$) so that only one photon is necessary for dissociation in the spectral range of our measurements (600 - 1700 cm^{-1}). The structure perturbation of the chromophore is considered to be negligible.

Irrespectively of which measurement technique is used, infrared multiphoton photodissociation or the messenger atom technique, the assignment of the vibrational frequencies turns out to be difficult and quantum chemical calculations are generally required. By using different methods, depending on their efficiency and quality, a good interpretation of the data can be obtained. In chapters 4, 5 and 6 comparisons between frequencies calculated with different theoretical methods and experimental data are presented.